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Hexagonal wheel formation through the hydrogen-bonded assembly of cobalt Pacman complexes**

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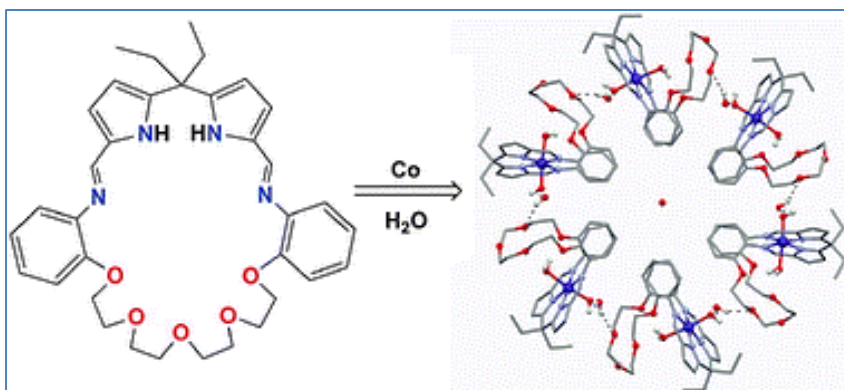
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Abstract

A cobalt aquo-hydroxo complex of a ditopic Schiff-base pyrrole – crown ether macrocycle has been prepared and forms a rigid Pacman-clefted structure that assembles through hydrogen-bonding into a hexagonal wheel motif in the solid state

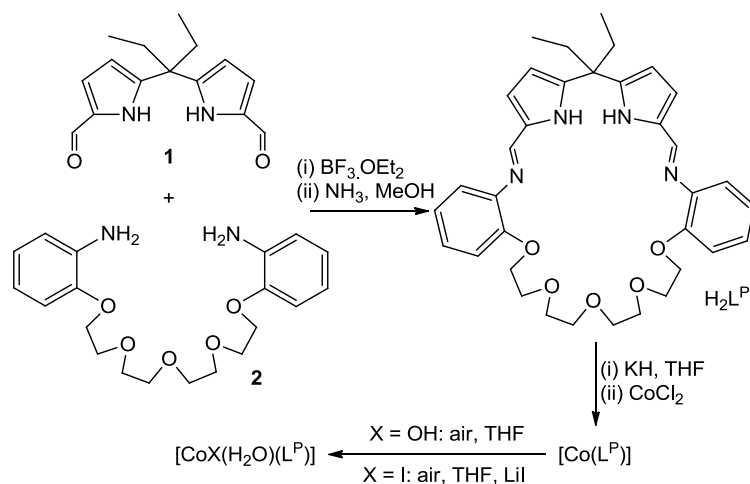
Main text

The design of frameworks that address both the primary and secondary coordination spheres of metal complexes and control the assembly of these metallo-tectons into targeted supramolecular structures is a difficult yet increasingly significant target. This is especially pertinent to technologically-important metal-catalysed reactions such as in oxygen and water interconversion, as it is clear that the mechanisms of proton and electron delivery affects the efficacy of metal catalysts in these reactions;^{1, 2} as such, an approach that builds downwards from the complexity of metalloenzymes towards the more simple constructs applicable to supramolecular catalysis is desirable.³ Ligands have been elegantly designed to tailor the metal reaction environment through the generation of deep cavities,⁴ second metal binding sites,^{5, 6} and/or acid/base or redox appendages,^{1, 7} while the provision of exogenous sites for hydrogen bonding or other supramolecular interactions has been used extensively to engineer higher order structures.^{8, 9}

We have shown previously that modular and simply-prepared Schiff-base pyrrole macrocycles H₄L containing two N₄-pyrrole-imine donor sets separated by two *o*-aryl hinges fold on metallation to form well-defined Pacman microenvironments and allow access to a wealth of d- and f-block redox chemistry, including catalytic oxygen reduction by cobalt complexes.^{5, 10} In contrast, metallation by Ln³⁺ cations resulted in interlinking, through exogenous coordination, of adjacent molecules into trimeric supramolecular wheels.¹¹ Significantly, mononuclear uranyl complexes of H₄L show unprecedented reactivity on manipulation of the vacant N₄-donor compartment,¹² chemistry that we have been unable as yet to investigate for transition metals due to an allosteric preference for bimetallic complex formation. As such, we report here a new, Schiff-base pyrrole macrocycle that incorporates N₄- and O₅-donor sets designed to provide both primary and secondary coordination sphere control in its monometallic Pacman complexes, and show how these features predispose Co complexes towards hydrogen-bonded supramolecular assembly.

The new O₅-donor compartment was conceived based on the aromatic diamine **2** tethered by an O₅ unit (Scheme 1) and is prepared from 1,2-(NO₂)(OH)(C₆H₄) in two steps in high yield. The [1+1] Schiff-base condensation reaction between dialdehyde **1** and diamine **2** proceeds efficiently and in good yield in the presence of BF₃(OEt₂) to form the new macrocycle H₂L^P after neutralisation with NH₃ in MeOH. In contrast

to the synthesis of H_4L ,⁵ cyclisation reactions in the presence of Brønsted acids such as CF_3CO_2H or $p-HOSO_2C_6H_4Me$ generated unidentifiable mixtures.



Scheme 1. Synthesis of the dual compartment Schiff-base pyrrole macrocycle H_2L^P and its cobalt complexes $[Co(L^P)]$, $[CoI(H_2O)(L^P)]$ and $[Co(OH)(H_2O)(L^P)]$.

The 1H NMR data for H_2L^P support cyclisation with a resonance at 8.24 ppm attributable to the imine protons and it is clear from resonances at 3.77 (4H), 3.60 (4H), and 3.50 (2 x 4H) ppm due to the ether backbone protons that the ligand is flexible in solution. The EI mass spectrum also supports the formation of a [1+1] macrocycle, with a molecular ion at 598 amu. Some very low intensity, higher weight ions are seen at 1198 and 1169 amu, which may indicate that higher cyclisation products are present; some broad resonances are also seen in the 1H NMR spectrum as shoulders to those of H_2L^P .

Reaction between $CoCl_2$ and in-situ generated K_2L^P in THF forms $[Co(L^P)]$ in good yield. The 1H NMR spectrum of $[Co(L^P)]$ displays 19 resonances between 69 and – 40 ppm consistent with a structure incorporating dissimilar ethyl groups, while the EI mass spectrum displays a molecular ion at 655 amu. The X-ray crystal structure of $[Co(L^P)]$ (Figure 1) confirms the presence of the Co(II) cation bound in the N_4 -donor pocket in a square planar geometry ($\sum \angle$'s at Co1 360.12°, Co1 0.042 Å out of N_4 -plane). Furthermore, the presence of the aryl groups between the N_4 - and O_5 -donor compartments promotes the expected wedge-shaped, or Pacman geometry, so positioning the O_5 -donor set above the Co- N_4 compartment. The lack of any endogenous ligand combined with the small size of the Co(II) cation allows the macrocycle to twist considerably, in a manner similar to that seen by us in the binuclear Co, Ni, and Cu chemistry of H_4L .⁵

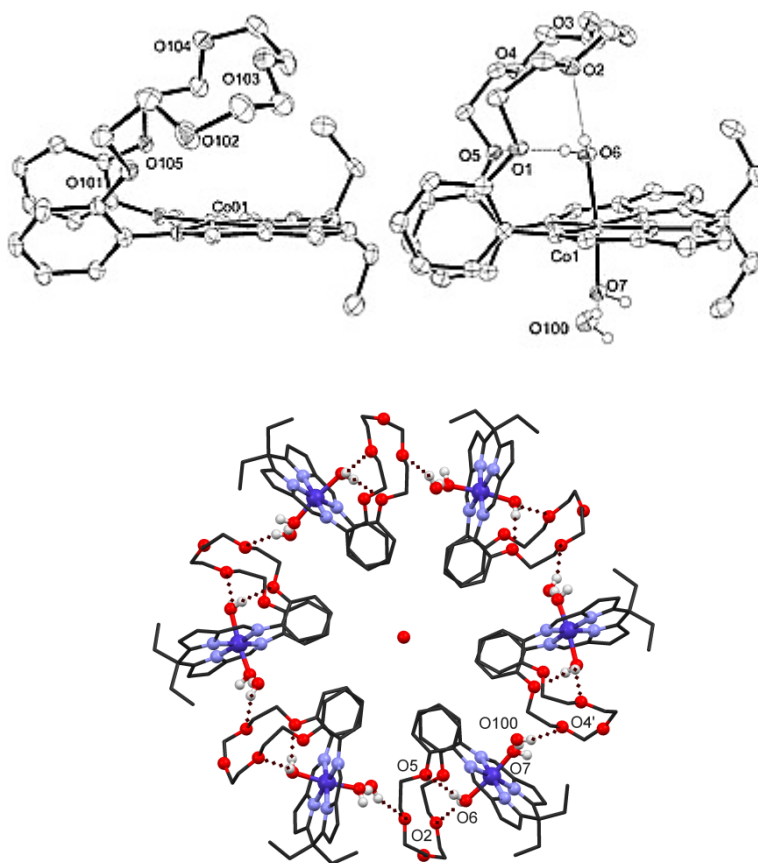


Figure 1. X-ray crystal structures of $[\text{Co}(\text{L}^{\text{P}})]$ (top left), $[\text{Co}(\text{OH}_2)(\text{OH})(\text{L}^{\text{P}})]$ (top right) and $[\text{Co}(\text{OH}_2)(\text{OH})(\text{L}^{\text{P}})]$ extended structure (bottom). For clarity, all hydrogen atoms except those located on O6, O7, and O100, and one molecule from the asymmetric unit of $[\text{Co}(\text{L}^{\text{P}})]$ are omitted (50% probability displacement ellipsoids where drawn).

Exposure of $[\text{Co}(\text{L}^{\text{P}})]$ to air in THF results in the formation of the Co^{III} complex $[\text{Co}(\text{OH}_2)(\text{OH})(\text{L}^{\text{P}})]$ as a result of spontaneous aerobic oxidation; the CV of $[\text{Co}(\text{L}^{\text{P}})]$ in THF under N_2 displays a quasi-reversible wave at -0.12V (Bu_4NBF_4 , Fc/Fc^+). The ^1H NMR spectrum in C_6D_6 displays resonances in the diamagnetic region consistent with a Pacman geometry, with two sets of resonances for the endo- and exo-meso-ethyl substituents and the proton resonances of the polyether backbone resolved into a series of multiplets that implies rigidity on the NMR timescale. The X-ray crystal structure of $[\text{Co}(\text{OH}_2)(\text{OH})(\text{L}^{\text{P}})]$ confirms the Pacman geometry, with, in the asymmetric unit, the Co centre pseudo-octahedral with the macrocyclic N_4 -donor set equatorial and H_2O and OH axial ($\text{O6-Co1-O7 } 173.67(10)^\circ$); the hydrogens on O6 and O7 were located from the difference Fourier map and refined with bond length restraints and riding thermal parameters. The molecule of water is bound within the macrocyclic cleft with a Co1-O6 bond distance of $2.033(2) \text{ \AA}$ and forms hydrogen bonds primarily to the polyether oxygen atoms O2 ($\text{O2}\cdots\text{O6 } 2.939 \text{ \AA}$) and O5 ($\text{O5}\cdots\text{O6 } 2.874 \text{ \AA}$) which results in a substantial decrease in the twist when

compared to $[\text{Co}(\text{L}^{\text{P}})]$; these observations are consistent with the increased structural rigidity observed by NMR spectroscopy. The OH group is bound to the cobalt (Co1-O7 1.880(2) Å) exogenous to the cleft and forms an intermolecular hydrogen bond to O100 of a molecule of water ($\text{O7}\cdots\text{O100}$ 2.669 Å) which in turn links the structure in the solid state through a hydrogen-bonding interaction to O4 of an adjacent molecule ($\text{O100}\cdots\text{O4}'$ 3.118 Å). These supramolecular interactions result in the assembly of the asymmetric unit into a hydrogen-bonded, crenallated cyclic hexamer in which adjacent Pacman molecules alternate above and below the median plane. Further expansion of the solid state structure reveals that each crenallated cyclic hexamer interlocks to form a columnar structure containing a channel of approximately 7.6 Å diameter (aryl C-H to C-H distance, see supporting information) that is occupied by water of crystallisation (approximately 4 molecules per cyclic hexamer); each column is further arranged in a hexagonal array (Figure 2). Void analysis using a spherical probe of radius 1.15 Å shows that the channels are accessible to water throughout their lengths. While localised electron density is present within the channels it could not be modelled satisfactorily and so it is likely a diffuse one-dimensional chain of water.¹³

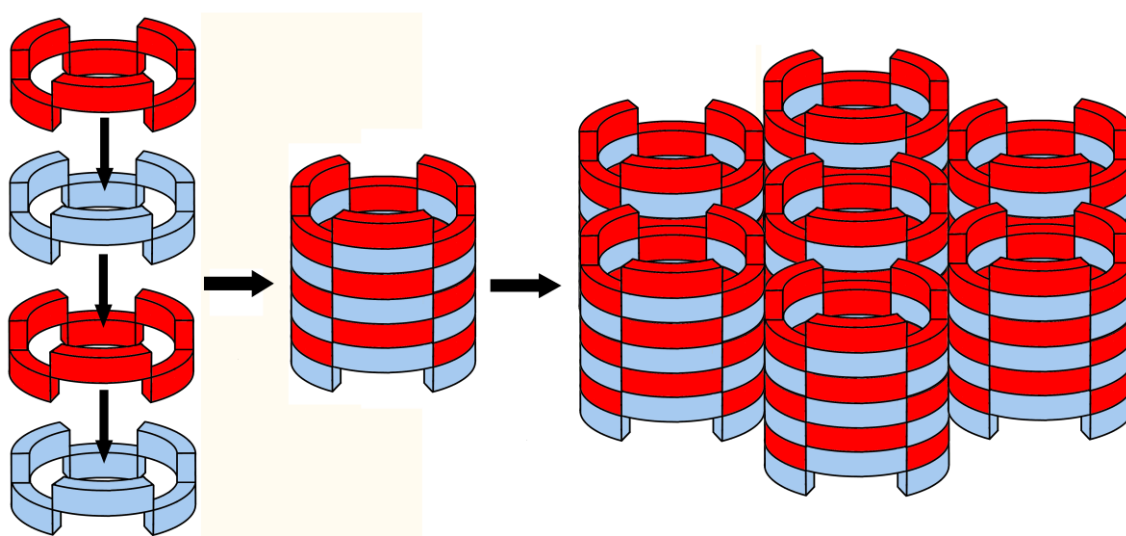


Figure 2. Representation of the extended X-ray crystal structure of $[\text{Co}(\text{OH}_2)(\text{OH})(\text{L}^{\text{P}})]$ where each ring crenallation represents one Pacman molecule in the cyclic hexamer linked at the corners by hydrogen bonding.

Several examples of the cyclic assembly of metal complexes through hydrogen-bonding have been reported including $[\{\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OH})\}_2]$ in which the pendant hydroxyl groups form a hydrogen-bonded $(\text{OH})_6$ ring similar to those seen in the structures of alcohols.⁹ Examples of wheel or giant-nanoring metal oxide or oxometallate structures constructed through bridging covalent interactions have been reported and

display interesting properties such as single molecule magnetism.¹⁴ Metal helicates have been shown to assemble through π -stacking in the solid state into hexagonally-packed circular structures with nano-sized channels.¹⁵ However, the assembly of *discrete* metal complexes into large, cyclic structures in which the metal complex retains potential catalytic function is rare; the catalytic chemistry of metal-organic-frameworks and their post-synthetic modifications is only recently becoming reported.¹⁶ A vanadyl salen complex forms a hexameric wheel structure in the solid state, in which weak $O=V\cdots O=V$ interactions link each monomer unit.¹⁷ Cyclic structures have also been generated by linking M(porphyrin) subunits through covalent interactions.¹⁸

Air-oxidation of $[Co(L^P)]$ in THF in the presence of LiI forms a mixture from which crystals of the complex $[Co(OH_2)(I)(L^P)]$ were isolated in which the OH^- ligand has been substituted by I^- . In the X-ray crystal structure,[†] the water molecule is coordinated similarly to $[Co(OH_2)(OH)(L^P)]$ within the molecular Pacman cleft and hydrogen bonds to the ethereal oxygens, with the iodide exogenous. The lack of a hydrogen-bond donor at the exogenous site has negated the evolution of a supramolecular structure; as such, it is clear that the exogenous hydroxyl group in $[Co(OH_2)(OH)(L^P)]$ is an important feature in the assembly of the hexameric wheel motif.

The stability of $\{[Co(OH_2)(OH)(L^P)]\cdot H_2O\}_6$ in solution was evaluated.[†] When dissolved in a 50:50 mixture of PhMe/CH₃OH, the ESI mass spectrum showed no evidence of the cyclic hexamer with ions at m/z 655 and 625 ($M^+ - 2Me$) for the cobalt complex $[Co(L^P)]$ and for its MeOH adduct at m/z 687 and Na and K adducts at m/z 679 and 695. In the ¹H NMR spectrum, addition of CD₃OD to a solution of the hexamer in C₆D₆ caused resonances due to the ethereal and meso-substituent protons to become less complex, suggesting a less rigid, potentially-monomeric structure is present. However, in the absence of protic solvents (CH₃CN), the monomer aggregates in solution with an ion at m/z 2019 consistent with the trimer $[\{Co(L^P)\}_3(OH)_2(H_2O)]^+$ in the cryospray mass spectrum. Ions were also seen for dimer and monomer, but no heavier ions were observed. ¹H NMR nOe data in C₆D₆ show clear intramolecular nOe and possible, albeit weak intermolecular nOe between aryl/imine and ethereal protons; however, some of these latter contacts remain on addition of CD₃OD so their identity is unclear. Overall, these data imply that the cyclic hexamer has limited stability in solutions containing protic solvents, but some aggregation does occur in their absence although the degree of aggregation remains uncertain.

We have shown that the new ditopic macrocycle H_2L^P forms wedged-shaped Pacman complexes of cobalt with environments suited to the binding of water within the molecular cleft. The exogenous hydroxide facilitates aggregation through intermolecular hydrogen-bonding of individual molecules into crenellated cyclic hexamers which stack further in the solid state into columns containing a diffuse water chain. The assembly of complexes into higher order cyclic structures is rare and represents a new motif for the design of supramolecular catalysts. We are currently looking to expand the scope of this assembly process towards more solution stable cyclic entities and to assess the effect of this supramolecular structure on catalytic activity.

Notes and references

‡Syntheses: $\text{H}_2\text{L}^{\text{P}}$ Yellow solid in 40 % yield (0.89 g). Found: C, 70.08; H, 6.94; N, 9.20. $\text{C}_{35}\text{H}_{42}\text{N}_4\text{O}_5$ requires: C, 70.21; H, 7.07; N, 9.36 %; $[\text{Co}(\text{L}^{\text{P}})]$ Red solid in 68 % yield. Found: C, 63.97; H, 6.08; N, 8.49. $\text{C}_{35}\text{H}_{40}\text{N}_4\text{O}_5\text{Co}$ requires: C, 64.12; H, 6.15; N, 8.55%; $[\text{Co}(\text{H}_2\text{O})(\text{OH})(\text{L}^{\text{P}})] \cdot \text{H}_2\text{O}$: Red crystals of $[\text{Co}(\text{H}_2\text{O})(\text{OH})(\text{L}^{\text{P}})] \cdot \text{H}_2\text{O}$ were grown from slow diffusion of hexane into an air-saturated benzene solution of $[\text{CoL}^{\text{P}}]$. Found: C, 59.28; H, 6.31; N, 7.95; $\text{C}_{35}\text{H}_{45}\text{CoN}_4\text{O}_8$ requires: C, 59.32 ; H, 6.40; N, 7.91 %

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